Crossover of the dimensionality of $3d$ spin fluctuations in LaCoPO

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We report the dc magnetization in the polycrystalline sample of LaCoPO in the range 4 - 300 K in presence of the external magnetic fields of 0.1 and 7 T. A comparison of the results in both fields suggest a spin fluctuation dominated ferromagnetically ordered state. The present ^{31}P NMR spin lattice relaxation data also supports this along with a clear indication of cross-over from 2D to 3D spin fluctuations across $T_{\rm C}$. The hyperfine field, ($H_{\rm hf}$) at the ^{31}P site is anisotropic in contrast to isotropic $H_{\rm hf}$ in LaFePO. This gradually reduces to zero near $T_{\rm C}$. The origin of anisotropy should be related to the magnetic moment arising from the $3d$ spins in case of LaCoPO.

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Newly discovered correlated electron systems LnT$_{\rm M}$PnO [Ln=$4f$ rare earth element, T$_{\rm M}$=transition metal element with more than half-filled $3d$ shell, Pn=pnictogen element] show interesting electronic and magnetic properties such as high transition temperature superconductivity, itinerant ferromagnetism, giant magnetoresistance, spin density wave (SDW) and structural instability[1]. In particular, LnFeAsO, exhibit pin density wave (SDW) and structural instability[2, 3, 4]. Moreover, they remain metallic to low temperature and only shows superconductivity ($T_{\rm c}$ in the range 26 - 55 K), when the SDW is suppressed towards zero temperature either through doping[5] or pressure[6]. In contrast, analogous phosphorous-based LaFePO, and LaNiPO are non magnetic metals and exhibit superconductivity ($T_{\rm c}$ in the range 2 - 6 K) due to strongly correlated electrons in the undoped form at ambient pressure, with the magnetic ordering being suppressed due to the reduction of magnetic moments[7, 9, 10, 11, 12]. It is be noted that ^{31}P NMR results in $(La_{0.87}Ca_{0.13})$FePO[13] suggests the presence of short range ferromagnetic correlations with no long range magnetic ordering down to 2 K. However, in case of LaCoPO, the magnetic moment does not vanish completely due to odd number of electrons in $3d$ orbitals. This system undergoes ferromagnetic transition near 43 K, when the magnetization is measured in an external field of 0.1 T, with no superconducting transition down to 2 K[8]. These results also suggest LaCoPO as an itinerant ferromagnet.

Recently, we presented ^{75}As NMR study in partially oriented parent and F-doped CeFeAsO system focussing the importance of $4f$ electron induced correlation effect over the obvious presence of the same due to $3d$ electrons[14]. In the present paper, we report the results of dc magnetization and ^{31}P NMR in LaCoPO. ^{31}P being a spin $1/2$ nucleus, the resonance line shape would be affected only by the magnetic interaction and hence offer the opportunity to obtain unambiguous information about the low temperature electronic state. We have also performed ^{31}P NMR study in LaFePO for comparison.

The present results in LaCoPO suggest a strong field dependence on the onset (temperature) of ferromagnetic ordering suggesting the dominance of spin fluctuations even in the magnetically ordered state. Nuclear spin lattice relaxation (T_1) data also confirms this with an indication of a crossover of the dimensionality of the ferromagnetic spin fluctuations near 130 K.

Polycrystalline samples of LaCoPO and LaFePO were synthesized by solid state reaction[7, 8] and were characterized using powder x-ray diffraction (XRD) with CuKα radiation at room temperature. The magnetic moment was measured with a SQUID magnetometer (MPMSXL 7 T, Quantum Design) in presence of the magnetic fields of 0.1 and 7 T. The NMR measurements were carried out in a conventional phase-coherent spectrometer (Thamway PROT 4103MR) with a H_0=7.04 T superconducting magnet. The powder sample of LaCoOP was aligned using epoxy (Epotek-301) in the magnetic field of 7 T.
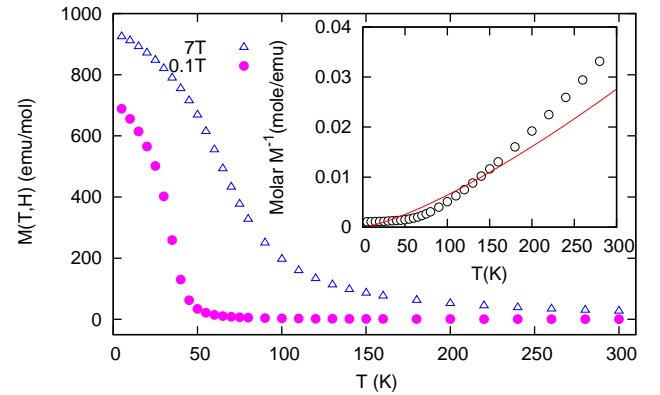

FIG. 1: (Color online) M Vs T curve at 7 T and 0.1 T. In the inset $1/M$ vs T curve is plotted and the solid line is of $T^{4/3}$ curve.

Fig. 1 shows the variation of the magnetic moment, M with temperature, in the field cooled and zero field cooled conditions, in presence of magnetic fields of H = 0.1 and 7 T. The results indicate the absence of any

irreversibility with a sharp enhancement of M below 50 K in a field of $H=0.1$ T, as reported earlier[8]. As the NMR measurements were done in a field of 7 T, the bulk magnetization was also measured in this field in order to compare the bulk and the local magnetic properties derived from the NMR results. It is clearly observed that in this field, the rapid enhancement of M due to the magnetic ordering starts at a much higher temperature (∼130 K) compared to that observed in a field of 0.1 T. Such strong field dependence of T_C is also reported recently in layered compound $La_{1.2}Sr_{1.8}Mn_2O_7$[15]. One possible reason for this could be the existence of spin fluctuations in the ordered state. Application of a field of 7 T would reduce the effect of fluctuation and favor the ordering of the spins at much higher temperature. This is also supported by the observation of negative magneto resistance in LaCoPO[8].
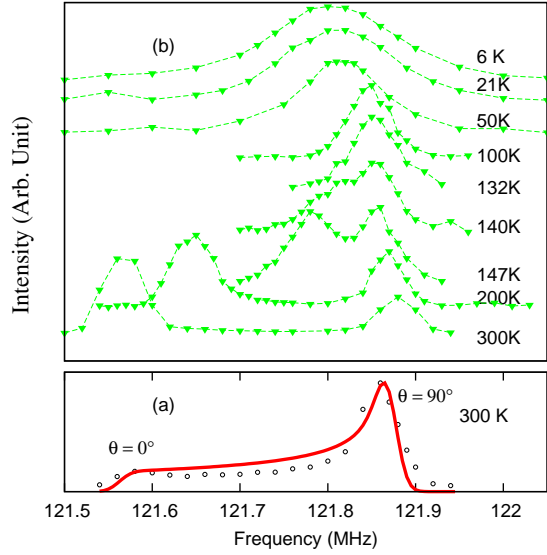

FIG. 2: (Color online) (a): Powder pattern of LaCoOP has also been shown by open circle in the lower panel along with the calculated spectrum represented by the continuous line. (b): ^{31}P NMR spectra in partially aligned LaCoOP sample taken at 7.04 tesla, dotted line is for guide to eye.

Fig. 2(a) shows a typical ^{31}P NMR spectrum in polycrystalline LaCoOP which is anisotropic in nature. This corresponds to the powder pattern for a spin 1/2 nucleus with axially symmetric local magnetic field, as expected for tetragonal symmetry. The step in the low frequency side corresponds to $H \parallel c$ ($\theta = 0°$) and the peak in high frequency corresponds to $H \perp c$ ($\theta = \pi/2$). The shift of the step with respect to the reference position (ν_R), corresponds to $K_\parallel$ and that of the maximum corresponds to $K_\perp$. In Fig. 2(b) we have presented spectra of partially oriented sample, where ∼60% of the grains are oriented in the direction of $H \parallel c$. As a result we have obtained two well resolved peaks in a same spectrum. Taking advantage of the partial alignment, $K_\parallel$ and $K_\perp$ can be determined accurately. This allows us to measure K_{iso} and

K_{ax} from the relations $K_{iso} = 2K_\perp/3 + K_\parallel/3$ and $K_{ax} = 1/3(K_\parallel - K_\perp)$. As the temperature is lowered the peak at $H \parallel c$ shifts gradually towards the high frequency side. Whereas, the peak at $H \perp c$ is shifted little towards the low frequency. Near 130 K, two peaks merge and start to broaden along with a small shift towards lower frequency. It is to be noted that this temperature corresponds to the onset of the ferromagnetic transition in LaCoPO in a field of 7 T (Fig.1). Merging of the two peaks suggests the vanishing of the anisotropy of the hyperfine coupling near 130 K. A weak temperature dependence of line position below 130 K, in the magnetically ordered state, together with a line broadening, is as expected in an ordered state. However, this broadening is not as high as it is in RFeAsO systems where there is a huge enhancement of ^{75}As NMR line width in the ordered state due to the spin density wave (SDW) transition. Whereas, in LaCoPO, the spectrum can be detected even at 4 K, which is well below T_C, suggesting a homogeneous ordered magnetic field along with an itinerant character of the Co $3d$ electrons responsible for the ordering. The latter corroborates the present bulk magnetization data (Fig.1). Fig. 3a shows the variation of $K_\parallel$ and $K_\perp$ as a function of temperature.
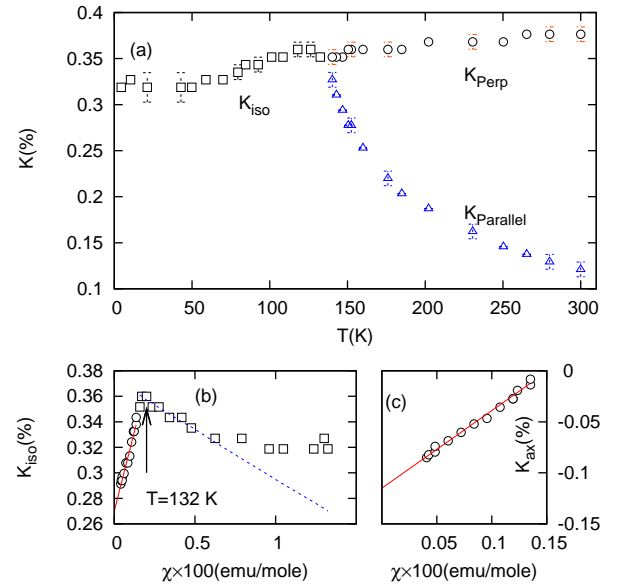

FIG. 3: (Color online) (a): Temperature dependence of ^{31}P NMR shift. (b), (c): Represent variation of K_{iso} and K_{ax} with χ respectively. The lines correspond linear fit.

The shift is mainly governed by the two contributions, one is due to conduction electrons (K_0), which is temperature independent, and the other is temperature dependent ($K(T)$) due to localized character of the d-electrons, such that $K_{total} = K_0 + K(T)$.

$$K(T) = H_{hf}^d \chi(T)/N_A\mu_B, \qquad (1)$$

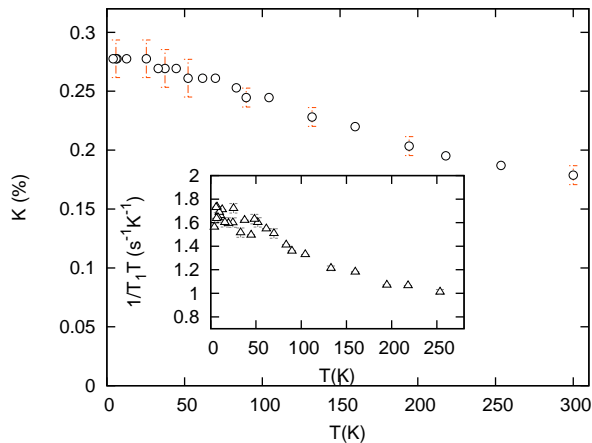where H_{hf}^d is the hyperfine field per μ_B. As long as

FIG. 4: (Color online) Variation of ^{31}P shift with T in LaFePO. Inset shows T dependence of $1/T_1T$ in LaFePO.

H_{hf}^{d} remains unchanged, $K(T)$ is proportional to $\chi(T)$. Fig. 3(b) and 3(c) show the variation of K_{iso} and K_{ax} with χ. Both the parameters show a linear variation in the range 130 - 300 K, with $H_{\text{hf}}^{\text{iso}} = 2.79$ kOe/μ_B and $H_{\text{hf}}^{\text{ax}} = 4.243$ kOe/μ_B The value of $H_{\text{hf}}^{\text{iso}}$ is found to be much smaller than that reported in case of Ca- doped LaFePO (H_{hf}=12.5kOe/μ_B[13]. A significant deviation of the K_{iso} vs χ plot linearity, below 130 K, indicates a modification of the electronic wave function contributing to the hyperfine coupling, responsible for the temperature dependent shift. There are two possibilities; one is the partial delocalization of the d-electrons due to mixing with the s-band near this temperature range, and the other is the crystal field effect. To compare the effect of complete replacement of Co by Fe, we have also performed the ^{31}P NMR study in isostructural LaFePO in the same temperature range in a polycrystalline sample. In this case a symmetric resonance line was observed throughout the whole temperature range with slow and gradual increase in line-width and shift (Fig. 4), and both of these parametrs becomes almost T independent below 50 K, as was reported earlier in Ca doped LaFePO[13]. This T independent behavior of K below 50 K in LaFePO (which does not exhibit ordering), is very similar to that in LaCoPO in the ordered state, in the same temperature region.

To verify the suggestion[8] that LaCoPO is an itinerant ferromagnet and the magnetic property should be governed by the spin fluctuations, we have measured T_1 at the peak corresponding to H∥c. The recovery of nuclear magnetization (Fig. 5) as a function of the product of the delay time (τ) and T follows single exponential in the range 4 - 300 K, as expected for a spin-1/2 nucleus. This also confirms the absence of any impurity contribution on ^{31}P NMR. Moreover, it clearly shows that T_1 decreases in the range 150 - 300 K and then increases till 100 K and stays constant if the temperature is further

lowered, signifying a metallic character. $1/T_1T$ (Fig. 6) shows a faster increment in the range 150 - 300 K compared to that in LaFePO, indicating the effect of slowing down of the 3d spin fluctuations due to the development of short range correlations above the magnetic transition temperature. The peak near 150 K suggests the development of long range correlations below this temperature. This gradually reduces the contribution of 3d spin fluctuations to the ^{31}P nuclear relaxation process, below 150 K. Finally an almost T independent behavior below 80 K signifies that the dominant role in the relaxation process is the Korringa contribution due to s-electrons and a less significant role of 3d spin fluctuations, as expected in a magnetically ordered state. Thus the present NMR result confirm microscopically the occurrence of a long range magnetic order in LaCoPO at a higher temperature in a field of 7 T, compared to that reported from magnetic susceptibility data at H=0.1 T. In order to understand the nature of the magnetic correlations we have analyzed the T_1 data using the existing theoretical models for the electron spin fluctuation contribution.

In general $(1/T_1T)_{\text{SF}}$ is given by[16]

$$(1/T_1T)_{\text{SF}} \propto (\gamma A_{\text{hf}})^2 \sum_q \chi''(q,\omega_n)/\omega_n, \qquad (2)$$

where $\chi''(q,\omega_n)$ is the imaginary part of the transverse dynamical electron-spin susceptibility, γ and ω_n are the nuclear gyromagnetic ratio and Larmor frequency, respectively. According to self consistent renormalization (SCR) theory of spin fluctuations, for weak itinerant ferromagnets (WIF), the ferromagnetic (q = 0) 3D spin-fluctuation contribution to $1/T_1T$ in presence of magnetic field, both in the paramanetic and the ferromagnetic region is given by the following relation[17, 18, 19]

$$1/(T_1T)_{\text{SF}} = k\chi/(1 + \chi^3 B^2 P) + \beta, \qquad (3)$$

where P is a constant related to the area of the fermi surface of the magnetic electrons and k is related to the energy width of the dynamical spin-fluctuation spectrum. β is temperature independent and contains the sum of the contributions due to orbital moments of p and d electrons, Fermi contact contribution of s conduction electrons and that due to the spin dipolar interaction with p and d electrons. Fig. 6 shows that the experimental curve deviates from Eq. 6 above 150 K and agrees in the range 80 - 150 K. So this relation is not satisfied in both the paramagnetic and the ordered state as it should[19]. According to the SCR theory of WIF [18, 20] $1/\chi$ or $1/M$ should vary as $T^{4/3}$. However it can be seen from the inset of Fig. 1 that above 150 K $1/\chi$ deviates from this relation which dictates that there is a crossover between 3D to 2D spin fluctuation near T_C. When 2D spin fluctuations are dominant,[13, 21, 22]
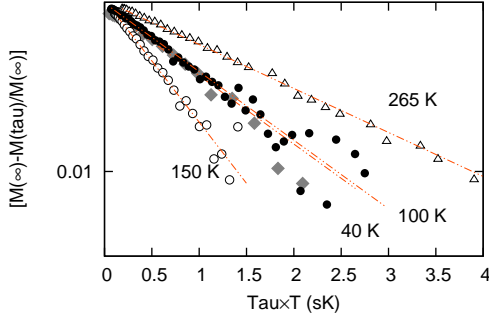
$$1/T_1T \propto \chi(q = 0)^{3/2}. \qquad (4)$$

FIG. 5: (Color online) Recovery curves Vs Tau ×T at different temperatures in LaCoPO, fitted with a single exponential.
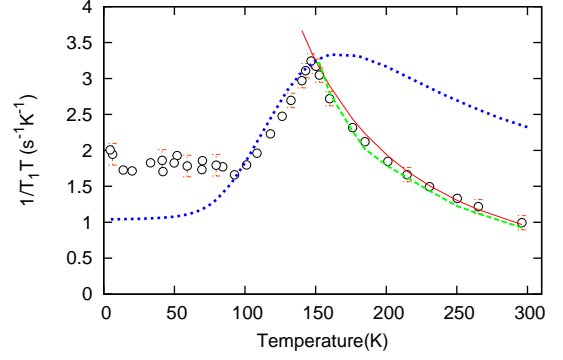

FIG. 6: (Color online) T dependence of $1/T_1T$ is represented by open circles in LaCoPO. Dotted line, dashed line and solid line correspond to equations (3),(4) and (5) respectively.

In the present case since K is proportional to χ in the temperature range 150 - 300 K (Fig.3a), so to calculate the value of $1/T_1T$ using Eq. 4 , we have used the values of K, since the Knight shift probes the intrinsic spin susceptibility of the sample, to see whether experimental $1/T_1T$ vs T curve follows the above relation. It is seen from Fig.6 that the experimental data agrees quite satisfactorily with the calculated curve in the above temperature range, which suggests the predominance of ferromagnetic 2D spin fluctuations above the ordering temperature. According to the extension of SCR theory for 2D itinerant ferromagnetic metal near magnetic instability[22]

$$1/T_1T \propto T^{-3/2}(-lnT)^{-3/2}, \qquad (5)$$

The calculated curve using Eq. (5) is also shown in Fig. 6. This also agrees quite satisfactorily with the experimental results and therefore further confirms the above conclusion. Since the spin fluctuation is 2D in nature above 150 K, the relaxation time should be greater than that in the case where 3D spin fluctuation dominates. Possibly this is the reason for the smaller value of T_1 obtained for the calculated value of $1/T_1T$ using Eq. (3) above 150 K. Thus we can conclude that their is a crossover from 2D to 3D ferromagnetic spin fluctuations from room temperature to low temperature through 150 K. Below 100 K, the relaxation process is mainly governed by the Korringa process. The $1/T_1T$ vs T curve for LaFePO is shown in the inset of Fig.4. The behavior is very similar to that reported in Ca-doped LaFePO. The slow but gradual increase of $1/T_1$ with T in the range 50 - 300 K could be a signature of the weaker short range correlations among the 3d spins of Fe in LaFePO compared to that in LaCoPO.

In conclusion, we report the dc magnetization in LaCoPO in the range 4 - 300 K in presence of 0.1 and 7 T. The results suggest the dominance of $3d$ spin fluctuations in the magnetically ordered state. This is further confirmed by the ^{31}P nuclear T_1 measurements. The T dependence of $1/T_1T$ in LaCoPO suggests the dominance

of 2D ferromagnetic spin fluctuations in the paramagnetic phase with a crossover to the 3D ferromagnetic spin fluctuation regime near the ordering temperature. In this compound, the hyperfine field is anisotropic at 300 K and it gradually reduces to zero near 130 K, below which the bulk susceptibility shows a sharp enhancement, due to the ferromagnetic ordering. On the other hand ^{31}P H_{hf} is isotropic in LaFePO in the range 4 - 300 K. The origin of the anisotropy in H_{hf} in case of LaCoPO could arise due to the larger magnetic moment of Co ion arising from the 3d-electrons, compared to very small magnetic moment of Fe ion in LaFePO, as revealed from a weak temperature dependence of shift K_{iso} and $1/T_1T$ in LaFePO in the range 50 - 300 K.

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